



RESEARCH

Water-in-Oil Emulsion Formation: A Review of Physics and Mathematical Modelling

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A literature review of the physics and modelling of water-in-oil emulsification is presented. The understanding of the physics of emulsion formation is still incomplete, but developing. The formation of emulsions is due to the surfactant-like action of polar compounds (resins) and asphaltenes in oil. These compounds act to maintain small (1–20 μm) droplets of water in oil. Volatile aromatic compounds in crude oils solubilize asphaltenes and resins. Crude oils containing lower quantities of these volatile compounds or BTEX (benzene, toluene, ethylbenzene, xylenes) will form emulsions given sufficient turbulent sea energy. Oils may lose the BTEX component by weathering before being capable of forming stable emulsions. The kinetics and energy of formation of emulsions is not well understood. Emulsions are often reported to form rapidly after the necessary chemical conditions are achieved and where there is significant wave action or other turbulent energy. Oil spill models generally employ a first-order rate law (exponential) to predict emulsion formation.

Keywords: Water-in-oil emulsification, asphaltenes and resins, BTEX.

Emulsification is the process of the formation of water-in-oil emulsions often called 'chocolate mousse' or 'mousse' among oil spill workers. Emulsification is a complication to the understanding of the fate of oil spills as well as to their clean-up. The formation of emulsions changes the properties and characteristics of spilled oil to a large degree. Stable emulsions contain between 60 and 80% water, representing an expansion in volume of spilled material from 3–5 times the original volume. The density of the resulting emulsion can be as great as 1.03 g ml^{-1} compared to a starting density as low as 0.80 g ml^{-1} (Fingas *et al.*, 1993). Most significantly, the viscosity of the oil typically changes from a few Pa.s (Pascal-seconds, a unit of viscosity) or less to about 1000 Pa.s, a typical increase of 1000. This viscosity increase changes a liquid product to a heavy, semi-solid material. This can render an oil spill difficult—if not impossible to clean up. For

these reasons, emulsification is felt by many to be the second most important behavioural characteristic of spilled oil after evaporation (Reed *et al.*, 1989). As a result of emulsification, evaporation slows by orders-of-magnitude, spreading slows by similar rates, and the emulsified oil rides lower in the water column, showing different drag characteristics with respect to the wind. This changes the outcome of oil spills to a very significant extent and therefore emulsification should be included in oil spill models.

The purpose of this review paper is to provide an overview of the research findings on the physics and chemistry of emulsion formation and subsequently how these same researchers suggest that the process be included in oil spill movement and behaviour models. This is not intended to be a critical review, or inclusive, but rather a summary of what the literature indicates about both the emulsion formation process and the modelling of this process. Often the results of several

research studies are in agreement and this is noted in the summaries and discussion sections of this paper.

Physics of Emulsification

The formation of water-in-oil emulsions by spills at sea was not noted until 25 years ago (Berridge *et al.*, 1968). This coincided with highly-publicized oil spills and the public concern over these events. Berridge and co-workers described emulsification and measured several physical properties (Berridge *et al.*, 1968). Berridge proposed that emulsions form as a result of asphaltenes and resins. Asphaltenes are large, polar compounds found in oil and are defined by the amount that precipitate when oil is dissolved in hexane or pentane. Resins are similar compounds but are believed to be smaller compounds and are also defined by precipitation techniques (Bobra, 1983). Workers in the 1970s concluded that emulsification occurred primarily with increased turbulence or mixing energy (Haegh & Ellingsen, 1977; Wang & Huang, 1979). Composition of the oil was not felt to be a major factor. Twardus (1980) found that emulsion formation may be correlated with oil composition. Asphaltenes and metal porphyrins were suggested as contributing to emulsion stability. Bridie and co-workers (1980) studied emulsions and proposed that the asphaltenes and waxes stabilized water-in-oil emulsions. Waxes are long-chain aliphatic compounds found in abundance in some oils. Mackay & Zagorski (1981, 1982a,b) hypothesized that emulsion stability was due to the formation of a film on the oil that resisted water droplet coalescence. The nature of these thin films was proposed to be due to the accumulation of certain types of compounds, later identified as asphaltenes and waxes. Lamathe (1982) conducted experiments on the formation of emulsions and found that photooxidation produced surface-active compounds suspected to be acids, attributed to be the cause of emulsion formation.

Thingstad & Pengerud (1983) found that photo-oxidized oil formed emulsions but unexposed oil did not. Nesterova and co-workers (1983) studied emulsion formation and concluded that it was strongly correlated with both the asphaltene and tar content of oil and also the salinity of the water with which it was formed. Mackay & Nowak (1984) and Mackay (1984) found that stable emulsions had low conductivity and therefore a continuous phase of oil. Stability was discussed and proposed to be a function of oil composition, particularly waxes and asphaltenes. Later publications by the same group reported Russian work which proposed that emulsions are stabilized by colloidal particles which gather at the oil-water interface and may combine to form a near-solid barrier that resists deformation and thus water-water coalescence (Stiver *et al.*, 1983). These particles, it was said,

could be mineral, wax crystals, aggregates of tar and asphaltenes or mixtures of these. Asphaltenes were felt to be the most important of these particles as they were felt to be instrumental in the formation of all particles. A formation equation relating the asphaltene, paraffin, aromatic and silica gel (resin) content was proposed.

Desmaison and co-workers conducted studies on Arabian crudes and noted that emulsion formation was correlated with two factors, photooxidation exposure and amount of asphaltenes (Desmaison *et al.*, 1984). The photooxidation was found to primarily affect the aromatic fractions of the oil and the compounds so formed appeared to increase emulsion formation. Asphaltenes were found to become structured with time and this was associated with emulsion formation. Miyahara (1985) reported that the stability of emulsions was primarily controlled by the composition of the oil, specifically that which resided in the hexane-insoluble fraction of the oil. Payne & Phillips (1985) reviewed the subject in detail and reported on their own emulsification experiments with Alaskan crudes in the presence and absence of ice. Their studies found that emulsion formation would occur in an ice field, thus indicating that there was sufficient energy even in this low-energy environment and that the process could occur at relatively low temperatures.

Mackay (1987) later proposed that the asphaltene particles gather at the oil-water interface and form a mechanical skin. This 'skin' was suggested to contain waxes, tar particles and other polar compounds. Microcrystals of wax were also hypothesized to stabilize emulsions. Thompson *et al.* (1985) studied a North Sea crude oil and noted that the thermal history of the oil was important in terms of emulsion stabilization. The smaller wax particle size formed by rapid cooling was attributed as the reason for an increased emulsion stability. Neuman and Paczynska-Lahme (1988) conducted studies on petroleum and water-in-oil emulsions. They concluded that petroleum itself is a micro-emulsion of asphaltenes and resins in an oil phase. Water-in-oil emulsions are attributed to the surfactant stabilization of asphaltenes and resins. Daling & Brandvik (1988) and Brandvik & Daling (1991) studied a series of emulsions noting that the water uptake kinetics approached a logarithmic form and that most oils took up the maximum amount of water in about 10 h. Eley *et al.* (1988) conducted a series of studies on emulsions and found that the maximum emulsification of water takes place when the asphaltene content is high and is preceded by a high aliphatic/aromatic ratio in the remaining oil. Water droplet diameters in emulsions were found to follow a log-normal distribution. The interfacial area or water uptake was found to follow a first-order rate law with respect to mixing time. Menon *et al.* (1988) studied the

formation of emulsions stabilized by fine mineral particles alone. Although these were possible, their stability was not as great as that of those stabilized by asphaltenes.

Sjöblom *et al.* (1990, 1992), Ebeltoft *et al.* (1992), and Urdahl *et al.* (1992) separated the polar, including the asphaltenic fractions, using a silica column and noted that all oils were incapable of forming emulsions after this separation. The separated fraction was found to contain fatty acids including palmitic acid. Environment Canada conducted a series of studies which focused on the physics of emulsion formation (Bobra, 1990, 1991, 1992). Those studies provided experimental results that show that emulsion formation is a result of surfactant-like behaviour of the polar and asphaltene compounds. The latter are similar compounds and both behave like surfactants when they are not in solution. The aromatic components of oil solubilize asphaltene and polar compounds. When there are insufficient amounts of aromatic components (about less than 3% volatile aromatics or BTEX) to solubilize the asphaltenes and polars, these precipitate and are available to stabilize water droplets in the oil mass. The minimum mass percentage of either asphaltenes or resins required to stabilize an emulsion was found to be approximately 3%. Droplet sizes of the water were measured using microscopy and were found to range from 1 to 20 μm . Nordli *et al.* (1991) studied various aspects of the interfacially-active resin and asphaltenic fraction, noting that this fraction is responsible for emulsion formation.

In summary, the literature shows that there is some understanding of the formation of water-in-oil emulsions. Related information on the kinetics of emulsion formation at sea and other modelling data are less abundant. The results of several independent studies show that emulsion formation is a result of surfactant-like behaviour of the polar and asphaltene compounds contained in the oil (Bobra, 1990, 1991, 1992). Both groups of compounds behave like surfactants when they are not in solution. Photooxidation results in polar compounds and these also contribute to emulsion formation. When there are insufficient amounts of aromatic components to solubilize the asphaltenes and polars, these precipitate and are available to stabilize water droplets in the oil mass. The minimum mass percentage of either asphaltenes or resins to stabilize an emulsion is about 3% (Bobra, 1990, 1991, 1992). Other components such as waxes, porphyrins, etc. do not appear to play a pivotal role. Emulsions begin to form when the above chemical conditions are correct and when there is sufficient sea energy. This energy is not measurable with current technology and its relative amount is not known in terms of emulsion onset. The literature indicates that the energy required to form emulsion varies (Daling & Brandvik, 1988; Brandvik &

Daling, 1991; Payne & Phillips, 1985). The rate of emulsion formation was investigated in some laboratory studies and was found to be first-order with time. This can be approximated with a logarithmic (or exponential) curve. Other studies noted rapid emulsion formation and a more step-like behaviour for emulsion onset (Payne & Phillips, 1985).

Modelling of Emulsion Formation

Little work on modelling of emulsion formation has been done. Most models that incorporate the phenomenon, use the estimation technique of Mackay (Mackay *et al.*, 1980; Mackay, 1980) or a variation of this:

$$\frac{dF_{wc}}{dt} = 2 \times 10^{-5} (W + 1)^2 \left(1 - \frac{F_w}{C_3} \right) \quad (1)$$

where dF_{wc}/dt is the rate of water incorporation, W the wind speed in m s^{-1} , F_w the fraction of water in oil, and C_3 the rate constant = 0.7 for crude oils and heavy fuel oils.

This equation is used in most models where emulsification is incorporated. Because the equation predicts that most oils will form emulsions rapidly given a high wind speed, most users have adjusted the equation by changing constants or the form slightly. The above equation is shown with constants from later workers (Reed *et al.*, 1989). Mackay & Zagorski (1982a,b) proposed relationships to predict the formation of emulsions on the sea. These were similar to the above. Huang (1983) proposed a linear relationship to predict the uptake of water. Rasmussen (1985) and Kirstein & Redding (1988) used variations of the Mackay equation above to predict emulsion formation. Reed *et al.* (1989) used the Mackay equations in several models. The constants were adjusted to be in line with field observations and are those presented above. The viscosity of the emulsion was predicted using a variant of the Mooney equation similar to that presented by Mackay *et al.* (1980):

$$\frac{\mu}{\mu_0} = \exp \frac{(2.5F_{wc})}{(1 - 0.65F_w)} \quad (2)$$

where μ is the viscosity of the mixture, μ_0 the oil starting viscosity, F_w the fraction of water in oil initially, and F_{wc} the final amount of water in the oil.

Several other workers in the field have used variations of the Mackay equations (Payne *et al.*, 1991; Spaulding *et al.*, 1992). The new ADIOS model incorporates a simple first-order rate law (Lehr *et al.*, 1992).

Most of the above work has basis in the Mackay equations which were developed before extensive work on emulsion physics took place. They have not been

correlated to either laboratory or field results. No studies showing the comparison of several models and field results have been published to date. Some of the above studies note real spills or field studies where emulsion formation is compared, but few quantitative results are given.

Summary

Several researchers indicate that both the tendency and the formation of emulsions could be predicted with a degree of accuracy using empirical data (Fingas *et al.*, 1993; Friberg, 1991; Aveyard *et al.*, 1991; Schramm, 1992). The formation of emulsions is known to occur when the asphaltenic and resin fraction combined exceeds 3% and the amount of the volatile aromatics or BTEX (benzene, toluene, ethylbenzene, and xylene) is less than this amount (Bobra, 1990, 1991, 1992; Fingas *et al.*, 1993). Since evaporation on the sea rapidly removes the BTEX component, prediction of formation could be approximated by predicted evaporative loss and the weight fraction of the asphaltenes and resins. When the latter rise over 3% and there is sufficient sea energy, an emulsion will form (Fingas *et al.*, 1993). There is insufficient empirical or theoretical information to predict the requirement for energy. Observations in the literature suggest that the energy requirement is variable, but that some oils will form emulsions at apparently low sea energies (Daling & Brandvik, 1988; Brandvik & Daling, 1991; Payne & Phillips, 1985).

Results from several researchers show that emulsion formation is relatively rapid and in the laboratory occurs fully—at moderate energies—in 3–10 h (Bobra, 1990, 1991, 1992; Fingas *et al.*, 1993). The rate may be first order with respect to time so an exponential function could be used to estimate formation rate. Other studies suggest that this may not be correct. A simplified approximation might be that emulsions form immediately given the correct oil composition and minimum required energy.

Further research is needed to fully understand the physics of emulsion formation, particularly that of the rate of the formation and the amount of energy required for formation. Models of emulsification are still at a crude state-of-the-art, however, they must await the data from new physical studies before they can be improved.

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